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980 nm electroluminescence from ytterbium *tris* (8-hydroxyquinoline)

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Abstract

We have demonstrated a ytterbium *tris* (8-hydroxyquinoline) based organic light emitting device giving sharp electroluminescence at ~980 nm, and demonstrated that it is not a requirement to match the energy of excitons formed on the organic ligands to those of the intra atomic transition within the ytterbium ion to obtain this emission. This may also be true for other rare-earth containing organic molecules thus allowing molecules to be designed for their charge transport properties rather than to match energy levels with the ions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of rare-earth containing organic molecules in organic light emitting devices (OLEDs) has been attracting increasing interest; due in part to the narrow emission lines which can be obtained, but also because of the possibility of obtaining improved efficiency over the more conventional materials [1–5]. As a result of this, much effort has been placed into designing rare-earth containing organic molecules whose highest occupied molecular orbit (HOMO) to lowest unoccupied molecular orbit (LUMO) energy separation match those of an intra atomic transition within a

rare-earth ion. There have been a number of reports on the use of rare-earths, such as europium and terbium which give visible emissions, but more recently there has been a growing interest in materials with infra-red luminescence, such as neodymium and erbium [6–9]. Possible uses for devices emitting in the infra-red include communications and gas sensing applications.

In this paper we investigate the photoluminescence and electroluminescence properties of ytterbium *tris* (8-hydroxyquinoline) (YbQ). Luminescence is observed around 1 μm , with a very sharp emission line at 977 nm, due to an intra-atomic transition from the $^2F_{5/2}$ to the $^2F_{7/2}$ level within the ytterbium ion. This wavelength is technologically important as it is the preferred pump wavelength for erbium doped optical fibre amplifiers. However, the energy of this transition does not match that of either the singlet or triplet

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excitons in this molecule. Given that this is the only such intra-atomic transition in ytterbium [10] it might be expected that coupling of excitons from the ligands to the ytterbium ion would be inefficient. One might therefore expect YbQ to show similar luminescence properties to that of AlQ with a bright ligand related visible luminescence and little emission from the ytterbium intra-atomic transition. The results presented here, however, show that such coupling does take place.

2. Experimental

The YbQ was synthesised by dissolving ytterbium chloride in deionised water and 8-hydroxyquinoline in an 80% methanol 20% deionised water solution. The first solution was then slowly added to the second whilst undergoing stirring at ambient temperature over a period of two hours. Further methanol was added and the solution left stirring overnight. The solution was then filtered and the remaining precipitate washed with methanol, at -25°C , to try and remove any remaining 8-hydroxyquinoline. The resulting substance was dissolved in methanol at ambient temperature and hexane was added until a fine precipitate was seen. The solution was then left in a freezer to cool before the precipitate was finally collected. Liquid chromatography was used to ascertain that only one material was present in the precipitate. Following this no further purification was undertaken before the YbQ was used.

Photoluminescence measurements were obtained from the bulk powder, a solution of YbQ in chloroform and from 200 nm films sublimed on to an aluminium coated silicon wafer. To obtain the photoluminescence of the bulk powder a small quantity was placed into a quartz cuvette. This, or one of the sublimed films, was placed inside a continuous flow cryostat which allowed the temperature of the sample to be set between 4 K and 300 K. Photoluminescence was excited using the 363 nm, 457 nm, 476 nm and 488 nm lines of an argon ion laser with the sample held at various temperatures. The luminescence was dispersed in a 1 m spectrometer using either a 1200 line grating, blazed at $\frac{1}{2}$ μm , or a 600 line grating, blazed at 1

μm , for the visible and infra-red luminescence respectively. To detect the luminescence a liquid nitrogen cooled Ge detector was used for the infra-red and an S-20 photomultiplier for the visible luminescence. All spectra were corrected for the response of the system and normalised to the excitation power used when exciting the photoluminescence.

When subliming the organic molecules onto silicon to produce the films and on to patterned, cleaned indium tin oxide coat glass to produce the OLEDs the base pressure was $\sim 10^{-6}$ mbar. The organic molecules were deposited at 1–3 $\text{\AA}/\text{s}$ and the diodes consisted of a 50 nm layer of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-3,3'-diamine (TPD) acting as the hole transporting layer and a 60 nm layer of YbQ acting as the electron transporting and emitting layer. The top electrodes consisted of a 200 nm thick layer of aluminium.

The OLEDs were operated d.c. using a Keithley 236 source-measure unit for all electrical measurements. The OLEDs were stored and operated in air for all experiments.

3. Results

Fig. 1(a) shows the 363 nm, 457 nm and 488 nm excited visible photoluminescence obtained at room temperature. It can be seen that as the excitation energy is increased the photoluminescence peak moves to a higher energy, from 2.08 eV (596 nm) for the 488 nm excitation to 2.58 eV (480 nm) for the 363 nm excitation. Accompanying this movement of the photoluminescence peak to a higher energy is a slight increase in the full width at half maximum (FWHM) of the spectra from 440 meV to 507 meV. Close inspection of the high energy tail of the 457 nm excited photoluminescence shows the presence of a peak which corresponds to that of the 363 nm excited photoluminescence. Given that this luminescence must originate from the organic ligands, this indicates that there are at least two energy levels within the chelate from which emission is possible. Also shown in Fig. 1(a) is the electroluminescence spectra obtained from a ITO/TPD/YbQ/Al OLED.

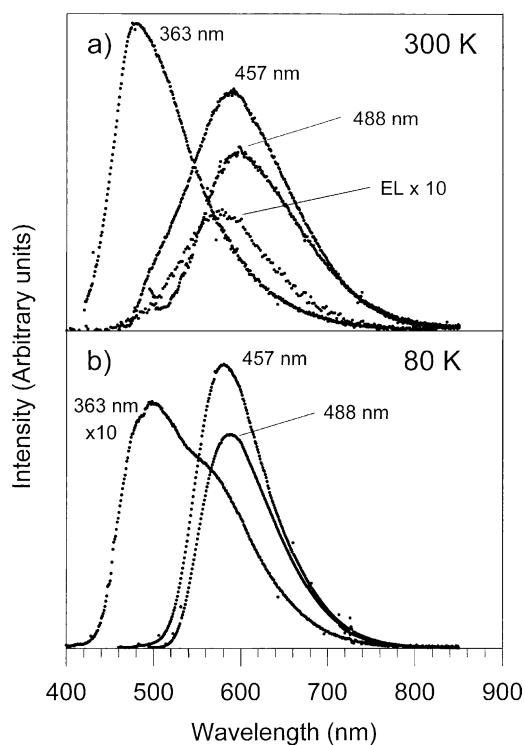


Fig. 1. (a) The visible photoluminescence of YbQ powder and electroluminescence of an ITO/TPD/YbQ/Al OLED obtained at 300 K. (b) The visible photoluminescence of YbQ powder obtained at 80 K.

Though the emission is weak it can be seen that the spectrum has a similar shape to that of the 457 nm and 488 nm excited photoluminescence. The peak of the electroluminescence is at 2.15 eV (576 nm) and it has a FWHM of 447 meV. Again this luminescence must originate from the recombination of excitons on the organic ligands.

Fig. 1(b) shows the 80 K photoluminescence spectra recorded under the same conditions as in Fig. 1(a). The most obvious effect of reducing the temperature on the 363 nm excited photoluminescence has been to reduce the intensity of the 2.58 eV emission relative to the emission from the lower energy level (2.08 eV) which corresponds to the emission level observed using the longer wavelength excitation. The effect of reducing the temperature on the 457 nm and 488 nm excited photoluminescence is to narrow the spectra from 498 meV to 343 meV and from 464 meV to 325

meV respectively. With this there is a slight movement of ~ 30 meV in the peak positions towards a higher energy. It can also be seen that the presence of the peak observed in the high energy tail of the 457 nm excited photoluminescence at 300 K has now vanished. This, along with the appearance of the second peak in the 363 nm excited photoluminescence, would suggest that any transfer of energy between these levels is limited by a thermal barrier. The narrowing of the 457 nm and 488 nm excited photoluminescence spectra is probably due to the reduction of phonon interactions as the temperature is reduced.

This behaviour is very similar to that observed for aluminium *tris* (8-hydroxyquinoline) (AlQ). We have previously shown [11] that the photoluminescence of AlQ originates from three levels within the chelate. One of these levels corresponds to the recombination of singlet excitons and the other two were suggested, from a model of the data, to be radiative recombination of triplet excitons. However, to accurately ascribe these levels to triplet recombination would require direct measurements of the lifetime of the transitions.

Fig. 2 shows the absorption spectra of YbQ in solution. With the shorter wavelength excitation we are directly exciting the singlet excitons; some of which can undergo intersystem crossing into triplet states but this transfer is probably small due

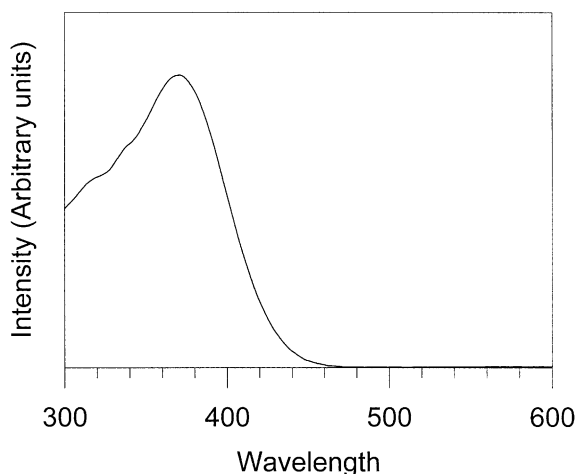


Fig. 2. The absorption spectra of 0.01 g of YbQ dissolved in 100 ml of dichloroethane.

to the short lifetime expected for these excitons. At longer excitation wavelengths, such as 457 nm and 488 nm, the absorption into the singlet state is very weak, Fig. 2, though there will still be some absorption of photons directly into the triplet state. This absorption into the spin-forbidden triplet state can occur due to the slightly mixed character of the states. However, the absorption will be weak and it is only the high excitation intensities used that allow us to observe it.

Due to spin-orbit coupling, which increases with the mass of the metal ion, there is some inter-system crossing between the singlet and triplet exciton states. At high temperatures the long lifetime of the triplet excitons means that some can cross into the singlet state resulting in the observed shoulder at ~ 2.5 eV (~ 480 nm). As the temperature is reduced, however, this crossing appears to be limited by a thermal barrier resulting in more radiative recombination from triplet excitons being observed. This corresponds to what is seen for the 363 nm excited YbQ photoluminescence in Fig. 1 as the temperature is reduced, with the singlet emission reducing in intensity relative to the triplet emission. Again this explains the 'loss' of the high energy peak observed in the 457 nm excited photoluminescence as the temperature is reduced.

Given the apparent similarity of this behaviour observed in YbQ to that observed in AlQ [10] it is not clear why the singlet recombination in YbQ should be so much weaker than in the group III quinolates. This difference has been noticed for other lanthanide quinolates such as erbium [7] and neodymium [9] and was thought to be due to competing non-radiative routes available with the introduction of the heavier metal ion. It may be that the larger ionic radius of the lanthanides compared to the group III ions increases the ligand steric strain and this may provide a non-radiative recombination mechanism. This suggestion is speculative and further work would be needed to understand the phenomena fully.

Fig. 3 shows the infra-red photoluminescence obtained from YbQ powder, a 500 nm film of YbQ on Si and a frozen solution of YbQ in chloroform. The photoluminescence of the powder and film, obtained using the 457 nm excitation, were recorded at 8 K in order to bring out the detail of the

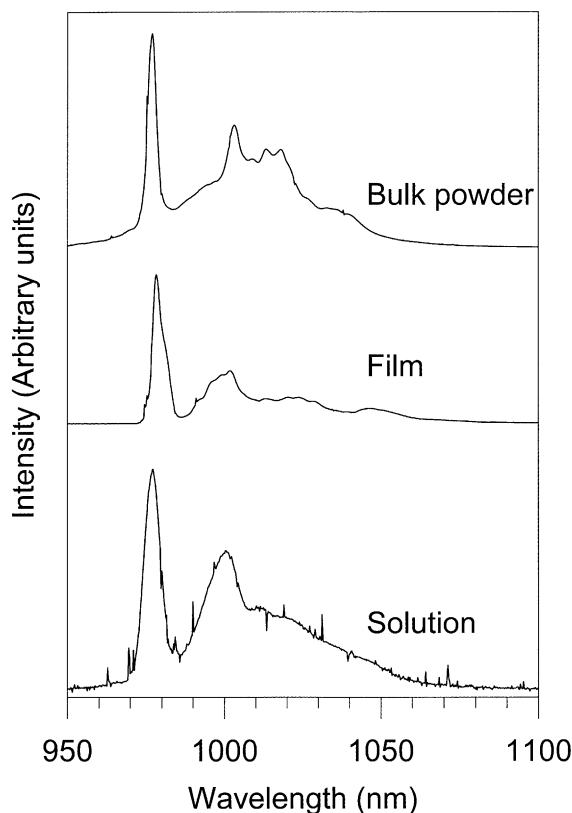


Fig. 3. The infrared photoluminescence obtained using an excitation wavelength of 457 nm for the bulk powder and a thin film at 8 K and for a solution of YbQ in CHCl_3 at 80 K.

Stark splitting of the intra atomic level in the ytterbium ion. The photoluminescence of the frozen solution was recorded at 80 K. Photoluminescence spectra obtained at room temperature were of similar intensity to the ones shown. This indicates that the transfer of energy from the ligands into the ytterbium ion is not a highly temperature dependent process.

It can be seen that the photoluminescence spectra differ quite significantly in detail. The photoluminescence of the bulk powder has a main peak at 977 nm and further peaks can be seen at 1003 nm, 1009 nm, 1013 nm, 1018 nm, 1026 nm, 1033 nm and 1040 nm. In the photoluminescence of the thin film however, the main peak has moved slightly to 978 nm and is slightly broader with the presence of another peak at around 980 nm being evident. Furthermore, the other peaks present

have also moved and changed in intensity when compared to the photoluminescence of the bulk powder. If there were only one isomer of YbQ, either C_1 or C_3 , then we would expect the Stark splitting of the $^2F_{5/2}$ level to give four peaks in the spectra [10]. If, as for AIQ, there were two possible isomers of YbQ, C_1 and C_3 , then this would raise the expected number of levels due to Stark splitting to 8. We can clearly see that the photoluminescence spectra show evidence of at least 10 levels and probably more. This would indicate that further splitting is occurring which could be due to the presence of neighbouring molecules altering the local symmetry seen by the ytterbium ions or coupling between optically active ions.

To investigate this further we measured the ytterbium related luminescence of a frozen solution of YbQ in chloroform at 80 K, Fig. 3. Here we can see that although the peaks are less well resolved, partly due to the higher temperature, the photoluminescence more closely resembles that of the sublimed films than the bulk powder. This result would not be expected if the YbQ in solution contained the same isomers as the bulk powder. It is possible though that the two isomers have different solubilities. This result may therefore suggest that it is structural effects that are responsible for the increased splitting and that the YbQ in the sublimed films may be in a more regular environment than those in the bulk powder.

Fig. 4 shows the electroluminescence spectra of a YbQ based OLED recorded at a drive voltage of 25 V, which corresponds to a current density of ~ 140 mA/cm². Though the electroluminescence is weaker in intensity compared to the photoluminescence, in part due to the lower concentration of Yb³⁺ ions available, it still has a strong main peak at 977 nm. It can be seen that the shape of the electroluminescence spectrum is very similar to the photoluminescence spectrum obtained from the sublimed film, as would be expected from the above argument.

For electroluminescence to occur at ~ 1 μ m there must be energy transfer from the chelate to the ytterbium ion. This energy must originate from the recombination of a singlet or triplet exciton on one of the organic ligands. The energy of a singlet exciton is indicated by the visible luminescence

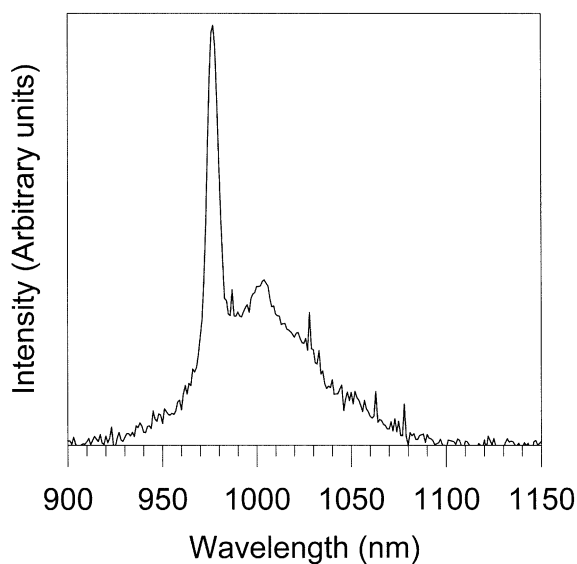


Fig. 4. The infrared electroluminescence of an ITO/TPD/YbQ/Al OLED obtained at 300 K driven at 25 V which corresponds to a current density of ~ 140 mA/cm².

observed which peaked at ~ 2.6 eV (~ 480 nm). The energy of any triplet excitons will be lower than this and if the photoluminescence observed when using the 488 nm excitation originates from the recombination of such excitons this gives an energy of ~ 2.1 eV. Due to the fact that Yb³⁺ is only one electron short of a full 4f shell, its energy level scheme consists solely of an inverted 2F level. This means that there are no energy levels above the $^2F_{5/2}$ level to couple the energy of the excitons on the organic ligands into. The energy of the $^2F_{5/2}$ to $^2F_{7/2}$ intra atomic transition within the ytterbium ion is ~ 1.27 eV. Given that the difference between the energy of the excitons on the ligands and the energy of this intra-atomic transition is of the order of 1 eV one might expect energy transfer between these states to be highly restricted. These results however show that this is clearly not the case for this system. Given that there are no higher energy levels for the exciton energy to couple into and then non-radiatively relax to the $^2F_{5/2}$ level, this implies that matching the energy of excitons formed on the ligands of organic molecules to the energy levels within rare-earth ions may not be as important as one would expect.

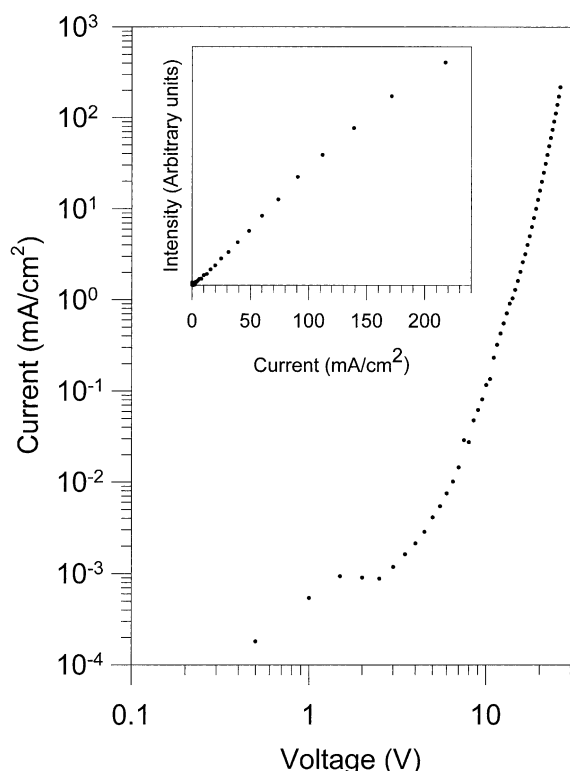


Fig. 5. The current–voltage characteristics of an ITO/TPD/YbQ/Al OLED. The inset shows the current–intensity characteristics of the same OLED.

Fig. 5 shows the current–voltage characteristic of the OLED operating in forward bias. Inset to Fig. 5 is the current–intensity plot for these diodes obtained at a wavelength of 977 nm. It can be seen that infrared emission occurs at current densities above ~ 5 mA/cm² which corresponds to a drive voltage of ~ 17 V. Also the current–voltage characteristics appear to be sub-linear. The cause of this apparent sub-linearity is not obvious. The effect is found to be reproducible on a given diode and hence we do not believe that it is indicative of device failure at high drive voltages. It could be that as many of the rare-earth transitions have long lifetimes, often from microseconds to milliseconds, we might be saturating the number of ytterbium atoms that are present in the exciton recombination region. However, given our device geometry and the density of ions present in the device we do not believe that this limit is being

reached. Another possibility is that as the drive voltage is increased we are getting the number of carriers transiting the device without contributing to the electroluminescence is increasing non-linearly. The exact cause of this sublinearity is still not understood and requires further study before being fully explained. The electrical behaviour of the YbQ diodes that we have constructed are very similar to those of both ErQ and NdQ devices [7,9], with both of these materials also exhibiting the sublinearity in intensity with current density. Our most recent results using oxygen plasma treated ITO substrates have shown that it is possible for the ErQ based diodes to decrease the turn on voltage for the diodes to ~ 5 V and to operate them at ~ 8 V. Given the similarities between the device structures we would expect to see similar performances for YbQ devices grown on the oxygen plasma treated ITO. Though no measurements of the efficiency of these devices were carried out typical values of the internal efficiency for ErQ devices were of the order of $\sim 0.01\%$.

4. Conclusion

In conclusion we have demonstrated a ytterbium based OLED giving electroluminescence at ~ 980 nm. We have also shown that it is not a requirement to match the energy of excitons formed on the organic ligands to that of the intra atomic transition within the ytterbium ion to obtain this emission. This may also be true for other rare-earth containing organic molecules thus allowing molecules to be designed for their charge transport properties rather than to match energy levels with the ions.

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